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The effect of rotating fields in magnetic resonance

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Abstract. The phenomenon of magnetic resonance is studied by considering the transverse oscillatory field as superposition of two oppositely rotating fields. One of the rotating fields is taken as strong and the other relatively weak.

Keywords. Magnetic resonance; rotating magnetic field; Bloch-Siegert shift.

1. Introduction

In most of the theoretical discussions on the transition rates of the relative population density in nuclear magnetic resonance, the transverse alternating magnetic field is taken to be a rotating magnetic field. The corresponding Schrödinger equation for any arbitrary magnetic moment has been solved exactly by Schwinger (1937). On the other hand, from the physical point of view a rotating field is to some extent an idealized one. In general, the phases of the transverse alternating magnetic fields may not be matched properly, in which case the transverse field consists of two rotating fields in opposite senses. The exact solution is not known in this case. However, a better approximation of the physical problem is to consider two rotating fields in opposite directions, the amplitude of one of which may be taken to be much stronger than the other. In such circumstances, since the exact solution with a single rotating field is known, we can consider the weaker rotating field as a perturbation and develop a perturbation expansion starting from the exact solution with the strong rotating field. The object of this paper is to develop such a perturbation expansion in the absence and presence of resonance, with arbitrary initial state and to study some of their important consequences. It is interesting to note that the treatment in the presence of resonance with a strong positively rotating field is quite different and much more involved than the case with a strong rotating field in the negative sense. The expressions for the relative population densities are obtained from the perturbation expansions developed in the paper.

One of the important physical consequences of the presence of an additional weak oppositely rotating field is the well-known Bloch-Siegert shift of the resonance frequency. Bloch and Siegert (1940) obtained the expression for the shift in an extremely involved manner and their method and result are strictly valid for only two levels which are resonating. But the results are applied quite frequently to multi-level systems which are in resonance. The method followed in this paper is not restricted only to two levels but is applicable to any finite number of levels in resonance. Further, it can be easily extended to resonances with multi-photon emission and absorption, observed by Brossel *et al* (1955). As a matter of fact our analysis shows that this shift of resonance frequency is a general property and is related to the ' intensity dependent frequency shift' in the scattering of electromagnetic radiation by free electrons (Sen Gupta 1949, 1952, 1966, 1967 and Eberly 1969). The shifts of resonance frequency are second order in the perturbation parameter, but it is well known that the conventional methods for obtaining the perturbation expansion leads to serious difficulty in the second and higher order terms due to appearance of secular terms in time, i.e. terms which increase indefinitely with time. The author (Sen Gupta 1970, 1972) has developed a more general type of perturbation expansion which has no secular terms so long as the time-dependent perturbation Hamiltonian is hermitian. The method followed in this paper is a further extension of the general perturbation expansion, in as much as the exact solution is known for a part of the time-dependent Hamiltonian and only the remaining time-dependent part is considered as a perturbation, as noted above. It may be mentioned that Seiden's expression (Seiden 1955) for the shift, though valid for arbitrary frequency, is strictly restricted for a single rotating field. In the experiments of ' optical pumping ', ' double resonance ' and ' radio-frequency spectroscopy of excited atoms ' the polarizations of the electromagnetic radiation play a very important role. Though the physical situations in these experiments are different due to the presence of strong polarized high frequency radiation which excites the atoms, the problem is almsot the same as discussed in the present paper if one is confined to the interaction of the magnetic fields between the magnetic sub-levels. Apart from the shifts observed by Brossel *et al* (1955) in multi-photon processes and by Brossel and Bitter (1952) a shift has recently been observed directly (Novikov and Mabyshev 1972). It may not be irrelevant to mention that by resonance, we restrict ourselves to resonance with the fundamental which is of relative physical importance; however, the method can be easily extended to resonances with higher harmonics.

Let the magnetic field be given by

$$\boldsymbol{H} = (h_x \cos \omega t,\ h_y \sin \omega t,\ \boldsymbol{H}_0) \tag{1}$$

so that the Hamiltonian may be written as

$$-\Omega L_z - \frac{\varepsilon}{2}\mathscr{L}_+ - \frac{\mu}{2}\mathscr{L}_- \tag{2}$$

where

$$\mathscr{L}_\pm = L_\pm\, e^{-i\omega t} + L_\mp\, e^{i\omega t},\quad L_\pm = L_x \pm i L_y \tag{3}$$

and

$$\Omega = \gamma \boldsymbol{H}_0,\ 2\varepsilon = \gamma(h_x + h_y),\ 2\mu = \gamma(h_x - h_y) \tag{4}$$

γ is the gyromagnetic ratio and $\boldsymbol{L}$ is the angular momentum operator in units of $\hbar$. $\varepsilon\mathscr{L}_+/2$ and $\mu\mathscr{L}_-/2$ are contributions to the Hamiltonian corresponding to the rotating magnetic field in the positive and negative senses respectively.*

In the next section, we briefly discuss separately the exact solutions with a single rotating field and the relative population density. The general problem is discussed in the following two sections separately. The case in which the rotating field in the negative sense is strong and the rotating field in the positive sense is weak (which is considered as a perturbation) is studied in section 3. In this case, the perturbation expansion is straightforward irrespective of the presence and absence of resonance. In section 4, we take up the case in which the rotating field in the positive sense is strong so that the weak negative part can be taken as a perturbation. In this case,

*The senses are relative to the choice of positive direction of z-axis, which is taken as the direction of the steady magnetic field.

the perturbation expansion in the presence of resonance needs special treatment. The last section is devoted to a short discussion on the methods used and the results obtained in the preceeding sections. Since the total angular momentum is constant, our state vectors belong to the subspace of a fixed j. Hence, j will not be explicitly mentioned except where it is necessary.

2. Case of a single rotating field

In this case, one of the terms in the Hamiltonian (2) is absent, $\varepsilon=0$ for positive sense and $\mu=0$ for the negative sense of the rotating field.

(i) *Single rotating field in the positive sense*

The Schrödinger equation in this case is

$$\mathrm{i}\frac{\mathrm{d}\Psi^{0}_{+}}{\mathrm{d}t}=-\left(\Omega L_{z}+\frac{\varepsilon}{2}\mathscr{L}_{+}\right)\Psi^{0}_{+} \tag{5}$$

i.e.

$$\left(\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}+\omega' L'_{z}\right)e^{\mathrm{i}\omega L_z t}\,\Psi^{0}_{+}=0 \tag{6}$$

where $L'_z=L_z\cos\theta'+L_x\sin\theta'$

and $\omega'=+\sqrt{(\Omega+\omega)^2+\varepsilon^2},\ \tan\theta'=\varepsilon(\Omega+\omega)^{-1}$ (7)

Hence,

$$\Psi^{0}_{+}(t)=e^{-\mathrm{i}\omega L_z t}\,e^{\mathrm{i}\omega' L'_z t}\,\Phi_0,\quad \Phi_0=\Psi^{0}_{+}(0) \tag{8}$$

This solution was given by Schwinger (1937). Let us expand the state Φ^0 in the basis of the orthonormal eigen states of L'_z, thus

$$\Phi_0=\sum_m a_m\varphi'_m,\quad L'_z\,\varphi'_m=m\varphi'_m \tag{9}$$

Since, the summations are always from, $m=j, j-1, \ldots\ldots 0 \ldots\ldots, -j+1, -j$, this will not be shown explicitly. The coefficients a_m are obtained from the initial state which is usually expressed in terms of the eigen state φ_m of L_z,

$$\Phi_0=\sum_m b_m\varphi_m \tag{10}$$

Since $$L'_z=\mathrm{e}^{-\mathrm{i}\theta' L_y}\,L_z\,\mathrm{e}^{\mathrm{i}\theta' L_y} \tag{7'}$$

from eq. (9) $$\varphi'_m=\exp\left(-\mathrm{i}\theta' L_y\right)\varphi_m=\sum_l \varphi_l\, d_{lm}(\theta') \tag{11}$$

so that $$a_m=\sum d_{mn}(-\theta')b_n \tag{12}$$

d_{mn} are the matrix elements of the reduced rotation matrix.* Hence, the state which evolves from an arbitrary initial state (eq. 10), is given by

$$\Psi^{0}_{+}(t)=\sum_m \overset{+}{B}_m(t)\varphi_m\exp\left(-\mathrm{i}m\omega t\right) \tag{13}$$

$$^{*}d_{nm}(\theta)=\sum_p\frac{\{(j+m)!(j-m)!(j+n)!(j-n)!\}^{1/2}}{(j+m-p)!(p+n-m)!(j-n-p!)p!}\times(\cos\theta/2)^{2j+m-n-2p}(\sin\theta/2)^{2p+n-m},$$

summation is over p with non-negative factorials only.

where $$\overset{+}{B}_m(t) = \sum \exp(i\omega' pt) d_{pq}(-\theta') d_{pm}(-\theta') b_q \tag{14}$$

The relative population density in the eigen state φ_m of L_z is $|\overset{+}{B}_m(t)|^2$. From eq. (14) it is simply periodic with period $2\pi/\omega'$ and does not contain any factor which is periodic with the period of the transverse rotating field. The average of $|\overset{+}{B}_m(t)|$ over cycles corresponding to the modified cyclotron frequency ω' is given by

$$\overline{|\overset{+}{B}_m(t)|^2} = \sum_{p,q,q'} d_{pq}(-\theta') d^*_{pq'}(-\theta') |d_{pm}(-\theta')|^2 b_q b^*_{q'} \tag{15}$$

In the special case of a pure initial state, say $b_l = \delta_{lq}$ this reduces to

$$|\overset{+}{B}_m(t)|^2 = \sum_p |d_{pq}(-\theta')|^2 |d_{pm}(-\theta')|^2 \tag{16}$$

(ii) *Single rotating field in the negative sense*

From eq. (3) it is clear that the rotating field in the negative sense is obtained by changing the sign of ω. Hence,

$$\Psi^0_-(t) = e^{i\omega L_z t} e^{i\omega'' L''_z t} \Phi_0, \ \Phi_0 = \Psi^0_-(0) \tag{17}$$

where $L''_z = L_z \cos\theta'' + L_x \sin\theta''$

and $\omega'' = \sqrt{(\Omega - \omega)^2 + \mu^2}, \ \tan\theta'' = \mu(\Omega - \omega)^{-1}$ (18)

so that all the previous results remain the same with θ'' replacing θ'. Therefore,

$$|\overset{-}{B}_m(t)|^2 = \sum_p |d_{pq}(-\theta'')|^2 |d_{pm}(-\theta'')|^2 \tag{19}$$

Hence, in both these cases the relative population densities are simply periodic with periods $2\pi/\omega'$ or $2\pi/\omega''$. However, in the second case the dependence of $|\overset{-}{B}_m(t)|^2$ on ω leads to a very sharp maximum. It follows from eq. (18) that

$$d\theta''/d\omega = 0 \text{ at } \Omega = \omega \tag{20}$$

This is the usual resonance condition. On the other hand with the rotating field in the positive sense $|\overset{+}{B}_m(t)|^2$ have no extremum with respect to ω as $d\theta'/d\omega$ from eq. (7) cannot be zero. It is clear from eqs. (8) and (17) that the above remarks about the dependence of $|\overset{\pm}{B}_m(t)|^2$ on ω are equally true with respect to the expectation value of any other observable for which the corresponding operator commutes with L_z, e.g. the average magnetic moment along the direction of the steady field.

3. Strong negative rotating field with weak positive rotating field

The Schrödinger equation is

$$i\frac{d\Psi_-}{dt} + \left(\Omega L_z + \frac{\mu}{2}\mathscr{L}_- + \frac{\varepsilon}{2}\mathscr{L}_+\right)\Psi_- = 0, \quad |\varepsilon| \ll |\mu| \tag{21}$$

Let us develop a perturbation expansion of Ψ_- with respect to the parameter ε, starting with the unperturbed solution (eq (17)).

$$\Psi_-(t) = \sum_{k,\,m} e^{i\omega L_z t}\, a_k \{\delta_{kl} + \varepsilon P^{(1)}_{km} + \ldots\}\, e^{im\omega'' t + i\varepsilon\rho_m t + \ldots} \times \varphi''_k \tag{22}$$

ρ_m are constants and $P^{(1)}_{km}$ are periodic (Sen Gupta 1970, 1972). We have retained only the first order term. For our problem $\rho_m = 0$ and

$$2P^{(1)}_{km} = \frac{L''_{+,\,km}(e^{-2i\omega t} - 1)}{\omega''(m-k) - 2\omega} + \frac{L''_{-,\,km}(e^{2i\omega t} - 1)}{\omega''(m-k) + 2\omega}, \tag{23}$$

where $$L''_{\pm,\,km} = (\tilde{\varphi}_k\, e^{i\theta'' L_y}\, L_\pm\, e^{-i\theta'' L_y}\, \varphi_m) \tag{24}$$

The matrix elements contribute only when $k-m = \pm 1$ or 0. It may be noted that for $3\omega \simeq \Omega$, the denominators may be very small and our discussion is restricted to the neighbourhood of resonance with the fundamental. Finally,

$$|\tilde{\varphi}_l\, \Psi(t)|^2 = \sum_{k,\,k',\,m,\,m',\,n,\,n'} e^{i(m-m')\omega'' t}\, d_{lk}(-\theta'')\, d_{lk'}(-\theta'')\, \{\delta_{km} + \varepsilon P^{(1)}_{km} + \ldots\} \times \{\delta_{k'm} + \varepsilon P^{*(1)}_{k'm'} + \ldots\}\, d_{m'n'}(-\theta'')\, d_{mn}(-\theta'')\, b_n b^*_{n'} \tag{25}$$

In this expression, apart from the exponential factor with ω'', $P^{(1)}_{km}$ are periodic with period $2\pi/\omega$ so that the time average is to be obtained by integrating over intervals which are large in comparison to both $2\pi/\omega''$ and $2\pi/\omega$. It is not difficult to see that there is no contribution to the average relative population density due to the first order terms in ε. It follows from the fact $P^*_{mn} + P_{nm} = 0$ from eq. (23), which is due to the hermiticity of the Hamiltonian. The first significant contribution is from ε^2 terms.

4. Strong positive rotating field with weak negative rotating field

The Schrödinger equation is the same as in eq. (21) except that now $|\mu| \ll |\varepsilon|$. But, in general, we cannot proceed as before because resonance may occur when

$$w' = 2w, \text{ i.e. } w = \Omega + \tfrac{1}{6}(\sqrt{16\Omega^2 + 12\varepsilon^2} - 4\Omega)$$

in which case the perturbation expansion is quite different. Since, in the absence of resonance the procedure is exactly the same as in the previous case and further, it is not of much physical importance we confine our discussions only with resonance. The unperturbed solutions in this case are given by the linearly independent solutions Ψ^0_+ (eq. (8)). Following the method developed by the author (Sen Gupta 1973) for the perturbation expansion with resonance, we write the expansion in powers of μ.

$$\Psi_+(t) = e^{-i\omega L_z t} \sum_{k,\,m} e^{i(m\omega' + \mu\eta_m + \ldots)t} \left(Q^{(0)}_{km} + \mu Q^{(1)}_{km} + \ldots\right) \varphi_k \tag{26}$$

$Q^{(0)}_{km}$, $Q^{(1)}_{km}$ are periodic. They are given by

$$Q^{(0)}_{km} = v_{km} \quad \exp\,[i(k-m)\omega t] \tag{27}$$

and $$Q^{(1)}_{km} = \sum_l{}' q_{kl}\, e^{i(l-m)\omega t}\, d_{lm}(\pi/2) g_m \tag{28}$$

$$q^{(1)}_{kl} = \frac{1}{4\omega} \left\{ \frac{L'_{+,\, kl}(e^{2i\omega t}-1)}{l-k+1} + \frac{L'_{-,\, kl}(e^{-2i\omega t}-1)}{l-k-1} \right\} \tag{29}$$

where

and

$$\left. \begin{aligned} L'_{\pm,\, km} &= \delta_{km} k \sin\theta' + \cos^2\theta/2 \cdot L_{\pm,\, km} + \sin^2\theta/2 \cdot L_{\pm,\, km} \\ g_l &= \sum_m d_{lm}(-\theta'-\pi/2) b_m \end{aligned} \right\} \tag{30}$$

The dash in the summation denotes that $l=k-1$ in the first term and $l=k+1$ in the second are to be omitted.* One can proceed similarly to obtain higher order terms in μ.

There are a few important features of the above solution, which are worth mentioning. Firstly, even in the presence of resonance it has no secular term, which increases indefinitely with time. This is also expected from the nature of the differential equation, namely eq. (21) with periodic hermitian Hamiltonian. Secondly, the starting unperturbed solution even for a pure initial state i.e. $|b_l|=\delta_{kl}$ is not a pure state but a mixture of states; it is a pure state only at $t=0$. Finally, apart from the factors exp $(i\omega' mt)$ and the coefficients Q_{km} which are periodic with the period of the oscillating field, they have exponential factors depending on $\mu\eta_m$. These factors themselves are also periodic but the period being inversely proportional to μ, is a few order larger than $2\pi/\omega$. The presence of these factors makes the problem of averaging over time relatively involved than that of the former case. The expression for the relative amplitudes is

$$\begin{aligned} B^+_m(t) = (\tilde{\varphi}_m \cdot \Psi_+(t)) = \sum_{l,k,q} \exp\,[i\{(2l-m)\omega + \mu\eta_l + (l-q)\omega'\}t] \times \\ \times \{\delta_{kl} + \mu q^{(1)}_{kl} + \ldots\} d_{lq}(\pi/2) d_{mq}(\theta') g_q \end{aligned} \tag{31}$$

In averaging $|B^+_m(t)|^2$ over a few cycles of the oscillatory field, we can neglect the variation with time of exp $[i\mu(\eta_l - \eta_{l'})t]$. It may be recalled that our perturbation expansion is valid only for $|\mu| \ll \Omega$ and $|\mu| \ll \omega'$. Proceeding as before with a pure initial state, i.e. $b_l = \delta_{lq}$, we get

$$\begin{aligned} |B^+_m(t)|^2 = \sum_{k,n} |d_{mk}(\theta')|^2 \{ |d_{nq}(-\theta'-\pi/2)|^2 \, |d_{kn}(\pi/2)|^2 + \\ + \sum_{n'}{}' e^{i\mu(\eta_n - \eta_{n'})t} d_{nq}(-\theta'-\pi/2) d_{n'q}(-\theta'-\pi/2) d_{kn}(\pi/2) d_{kn'}(\pi/2)\} \end{aligned} \tag{32}$$

In this expression we have not shown the dependence of the amplitude on μ, which is very small as the first significant term is proportional to μ^2. Though, our expressions are exact for all orders of ε, in practice the effective contribution to the matrix elements of the reduced rotation, $d_{nq}(\pi/2+\theta') d_{nq}(\theta')$ are only from the diagonal elements and the elements adjacent to them. This is due to the fact that $|\varepsilon|$ is also small in

*The secular equation in this case is

$$\sum_l \{(\sin\theta' - \eta_m)\delta_{kl} + \cos^2\theta/2\, L'_{x,kl}\}\, v_{lm} = 0$$

Hence, $\{v_{lm}\}$ for a fixed m is nothing but the eigenfunction of L'_x which is exp $[-\frac{1}{2}i\pi L'_y] \cdot \varphi_m$

comparison to Ω (eq. 7). Apart from the slowly oscillatory terms, $|B_m^+(t)|^2$ in eq. (32) has also a steady part. Although, unlike the previous case of resonance, it has no sharp maximum, the order of the quantities involved is not widely different.

5. Discussion

It is clear from the above that in both the cases with fields as in section 3 and 4 resonance may occur. Their difference is more of a quantitative than of qualitative nature. However, it should be emphasized that there is a small difference in the two resonance frequencies. In the first case with a strong negatively rotating field, from eq. (20) the resonance takes place exactly at $\omega = \Omega$. But in the second case from eq. (25) it occurs at

$$\omega = \Omega \left\{ 1 + \frac{2}{3} \left(\sqrt{1 + \frac{3}{4} \frac{\varepsilon^2}{\Omega^2}} - 1 \right) \right\} \tag{33}$$

The difference in the resonance frequencies for the two cases are,

$$\Delta \omega \simeq \frac{1}{4} \frac{\varepsilon^2}{\Omega^2} \; (\text{for } |\varepsilon| \ll \Omega) \tag{33'}$$

The shift of frequency in eq. (33) though basically of the same nature as the Bloch-Siegert shift, is different from it as we have considered above only the extreme case. This shift of resonance frequency has been observed recently by Novikov and Malyshev (1972).

In the above investigations, we have chiefly confined to the expressions for the relative population densities, but most of our results can be easily extended to the expectation values of operators which do not depend explicitly on time. Finally, since the interactions of positively and negatively rotating field in magnetically and optically active chemical substances are different, it may be of some interest to investigate both theoretically and experimentally, the effect of the two types of oscillating field on magnetic resonance experiments.

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